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Lithium Batteries Session

THE EFFECTS OF THE ELECTROCHEMICAL DESIGN UPON THE SAFETY AND PERFORMANCE OF THE LITHIUM-SULFUR DIOXIDE CELLS.

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Previous studies¹ have shown that the electrochemical balance between the anodic and the cathodic reactant affects the performance of the cell with regards to safety when it is overdischarged. Others² have reported data on the forced overdischarge of cells, but they did not consider cell balance.

Prior studies also showed that when excess lithium is present, a reaction occurs between lithium and acetonitrile upon the depletion of the sulfur dioxide. This leads to the formation of methane,¹ lithium cyanide and B-imino-n-butyrone.³ This condition was found in overdischarged cells having excess lithium. This is in contrast to the following reactions that occur during the normal discharge of lithium-sulfur dioxide cells:



These investigations include a wider range of lithium-sulfur dioxide ratios, especially in the lower portion, that is, at the stoichiometric ratio of one and less.

Experimental Procedures and Methods

These experiments were performed under forced overdischarge conditions, simulating an inferior cell situated in a series connected battery. The effects of the lithium-sulfur dioxide ratios, carbon content, rate of discharge and temperature were observed.

The cells employed for the measurements were of the D and squat-D type. They were constructed in a spirally-wound configuration consisting of a lithium anode, a polypropylene separator, and a carbon cathode; the electrolyte-reactant mixture was composed of sulfur dioxide, acetonitrile, and lithium bromide. The cell closure employed was a hermetic glass to metal seal. More detailed descriptions of the cell components have been previously reported.^{4,5}

The cells were discharged at constant current, while the cell voltage and temperature were monitored continuously. The thermocouple, used for the temperature measurements, was calibrated against a mercury thermometer and attached to the outside steel casing of the cell. Asbestos sheet was then wrapped around the cell, and the complete package was placed in a steel container. A standard (TB/2) environmental chamber was used for the low (-40°C) and the high temperature (71°C) discharge of cells.

The complete test plan is shown in Table I.

Results and Discussion

The experiments were performed to evaluate the capability of lithium-sulfur dioxide cells to safely operate especially under

TABLE I
TEST PLAN

Ratio	Current	Temperature	Carbon Capacity	Storage at 71°C
0.92	0.5-6A	RT, 71°C	10.9	—
1.0	0.5-6A	RT	13.0	—
1.2	1.0, 2.0	RT	9.1	—
1.3	0.25-1.0	RT	10.6	—
1.38	0.35, 2, 3	-40, RT, 71°C	12.1	YES
1.7	0.25-1.0	RT	10.9	—
2.0	0.5, 1.0	RT	—	—

forced overdischarge. The effects of the following variables will be discussed, which include the coulombic (stoichiometric) ratio of the lithium to sulfur dioxide, the discharge current and temperature, carbon cathode, and prior storage conditions.

The most significant variable in designing a cell capable of operating safely at high rates was found to be the lithium-sulfur dioxide stoichiometric ratio. Figure 1 shows a comparison between two cells having a ratio of 1.38 and 2.0, discharged at 2A. Curve 2 depicts the cell having the higher ratio which was achieved by loading the cell with less than normal quantities of electrolyte equivalent to 7.5 Ah of sulfur dioxide, hence, the electrical capacity attained was only 2.6 Ah to 2 volt cut-off. The temperature curve (the dashed line) shows an expected peak upon cell polarization and another occurred while the cell was in voltage reversal. The latter peak was due to a

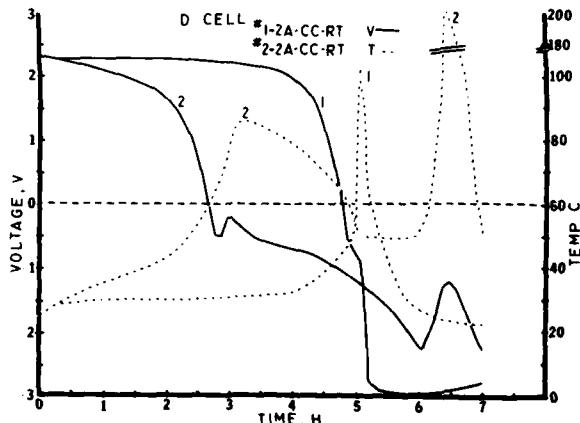


Figure 1. Voltage and Temperature for Complete 2A Discharge of "D" Cells with Different Li/SO_2 Ratios: #1—1.38, #2—2.

TABLE II
REPRESENTATIVE SUMMARY OF CELL DATA

Cell Type	Ratio Li/SO ₂	Current A	Temp. °C	Theor. Carbon Capacity (Ah)	Avg. Cell Capacity (Ah)	Storage Wks. 71°C	Qty. Cells	Remarks
D	0.92	0.5	RT	10.9	6.9	—	2	NORMAL ^(A)
		1.0	RT	10.9	7.3	—	2	NORMAL
		2.0	RT	10.9	7.4	—	5	NORMAL
		3.0	RT	10.9	5.2	—	4	NORMAL
		3.0	RT	10.9	5.7	—	1	VENTED ^(B)
		4.0	RT	10.9	4.3	—	2	NORMAL
		5.0	RT	10.9	6.0	—	1	NORMAL
		5.0 (Fig. 3)	RT	10.9	3.0	—	1	VENTED
		6.0 (Fig. 3)	—	10.9	2.2	—	2	VENTED, FLAME ^(C)
		3.0 (Fig. 2)	71	10.9	5.6	—	2	VENTED
		3.0	71	10.9	5.7	—	2	NORMAL
		8.0	—	13.0	—	—	2	VENTED, FLAME
		1.0	RT	13.0	8.3	—	2	NORMAL
1.0	1.0	2.0 (Fig. 5)	—	13.0	7.8	—	2	NORMAL
		4.0	—	13.0	5.0	—	2	NORMAL
		6.0	—	13.0	2.4	—	2	VENTED
		8.0	—	13.0	—	—	2	VENTED, FLAME
		1.2	—	9.1	8.5	—	2	NORMAL
Sq-D	1.3	0.25	—	10.6	9.4	—	2	NORMAL
		0.5	—	10.6	9.6	—	2	NORMAL
SQ-D	1.0	—	—	10.6	9.2	—	2	NORMAL
D	1.0	2.0 (Fig. 5)	—	9.1	2.9	—	2	VENTED, FLAME
SQ-D	1.38	0.35	-40	12.1	5.6	2	3	NORMAL
SQ-D	2 (Fig. 1)	RT	—	12.1	8.0	—	4	NORMAL
SQ-D	2	—	—	12.1	8.8	—	3	VENTED, FLAME
SQ-D	2	71	—	12.1	6.1	—	1	NORMAL
SQ-D	2	—	—	12.1	6.0	—	1	VENTED, FLAME
SQ-D	3	RT	—	12.1	5.8	—	2	VENTED, FLAME
SQ-D	3 (Fig. 2)	—	—	12.1	5.8	—	1	VENTED
SQ-D	3	71	—	12.1	5.3	—	3	VENTED, FLAME
SQ-D	3	—	—	12.1	4.2	2	1	VENTED
SQ-D	3	—	—	12.1	5.0	2	2	NORMAL
SQ-D	3 (Fig. 4)	—40	—	12.1	1.5	2	2	VENTED, FLAME
D	1.7	0.25	RT	10.9	9.4	—	2	NORMAL
		0.5	—	10.9	9.3	—	2	VENTED, FLAME
		1.0	—	10.9	8.3	—	2	VENTED, FLAME
		2.0	—	—	8.3	—	2	VENTED, FLAME
		1.0	—	—	8.1	—	3	VENTED, FLAME
		2.0 (Fig. 1)	—	10.9	2.6	—	2	VENTED, FLAME

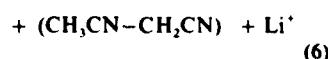
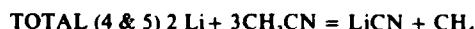
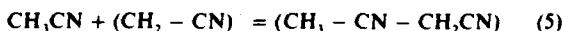
A—CELL OPERATED SAFELY THROUGHOUT THE DISCHARGE.

B—CELL VENTED DURING VOLTAGE-REVERSAL.

C—CELL VENTED WITH FLAME DURING VOLTAGE REVERSAL.

series of exothermic chemical reactions, previously investigated,¹ which were found to occur in a sulfur-dioxide starved environment. They are as follows:

SIDE REACTIONS: DEPLETED SULFUR DIOXIDE CONDITION



The heat of reaction for Eq (6) was found to be exothermic and calculated to be approximately 160 kilocalories. Even though less than 0.2 moles of acetonitrile are present in the cell, an appreciable temperature rise would be expected if it completely reacted. In the analysis⁶ of cells having a Li-SO₂ ratio of 1.4 and overdischarged at 500 mA and 1A, the two products stated in Eq. 6, methane and cyanide, were detected in the hundreds of milligram range. However, in cells with a ratio of 0.92, the quantity of these products was found to be 0.1 mg after six hours in voltage reversal at 500 mA. Another source of cell heating was the reaction between methane and sulfur dioxide⁷ at 130°C or higher; the complete overall reaction is as follows:

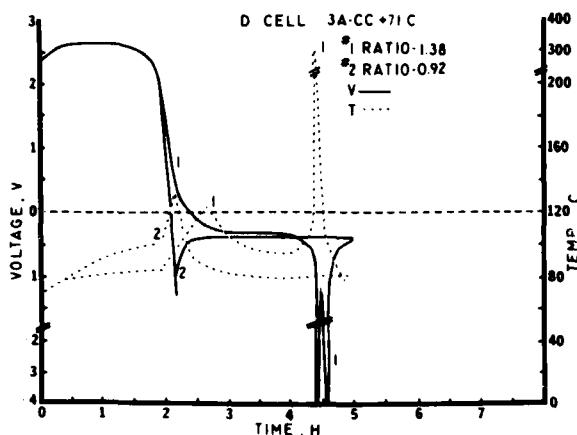
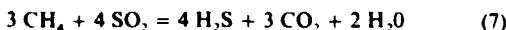


Figure 2. Voltage and Temperature for Complete 3A Discharge of "D" Cells with Different Li/SO₂ Ratios starting at 71°C.



Cells discharged at high rates did give the hydrogen sulfide odor when they vented in a violent manner.

In addition, the electrochemical deposition of dendritic lithium is highly probable when the cell potential is between zero and -2 volts (and anodic lithium is present). Due to the fact that at these current densities (~4 mA·cm⁻²) only cathodic polarization is expected, the cathode potential would be at a favorable level for lithium deposition. Further evidence of cathodic lithium has been obtained from cell post-mortems. Curve 1 (Fig. 1) shows a peak temperature of 120°C which also reflects a small degree of chemical reaction. Other cells having the same ratio have attained much higher temperatures during overdischarge at the same current; these cells vented with and without flame indicating cell instability (see Table II).

To determine the cell operating safety at higher rates and elevated temperatures (Figure 2) the current was increased

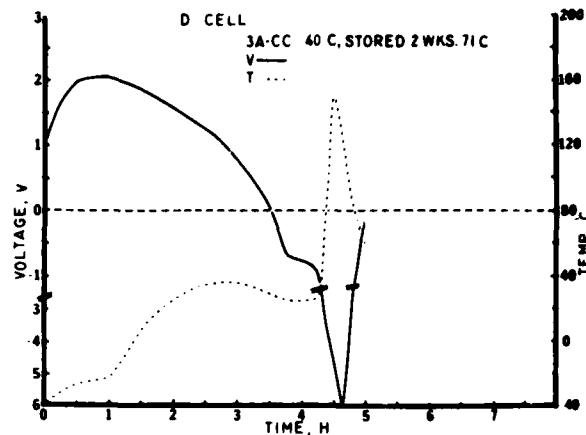


Figure 4. Voltage and Temperature for Complete 3A Discharge of "D" Cell with Li/SO₂ Ratio of 1.38 starting at 40°C.

to 3 amps while the ambient temperature was 71°C. The cell having the higher ratio of 1.38 (curve 1) displayed a cell potential of -0.4 volts for 1.75 hours before dropping rapidly. Hence, the conditions which have been described for cell 2 of Figure 1 are applicable for explaining the high peak temperature causing the cell to vent with flame. The cell having a ratio of 0.92 (curve 2 of Fig. 2) underwent a rapid decrease in voltage upon cell polarization due to the depletion of lithium; peak temperature was only 127°C at this current.

Other examples of a lithium-limited cell design are shown in Figure 3. Two cells were discharged at a constant current of 5 and 6 amps. With each cell a rapid polarization was observed caused by both anodic and cathodic limitations. The peak temperatures were 130°C at 5 amps and 220°C at 6 amps; only under the higher discharge rate was flaming observed. Cells (Table II) having greater carbon capacity only vented at 6A. Other cells from 0.5 through 4 amps were discharged. These cells, as expected, attained lower peak temperatures as the current decreased, and displayed a rapid voltage polarization due to anode limitations (see Table II).

The effects of high temperature storage (71°C) upon the operational cell safety was found to be ambiguous. In Figure 4 a cell having been stored for two weeks and with a ratio of 1.38 was forced overdischarged under 3 amps at -40°C. The low temperature was specifically chosen in order to subject the cell to a rather severe operating test; while a ratio greater than one was selected to examine mainly the effects of storage. The cell reached a high temperature of 155°C and vented. Other cells which have been exposed to high temperature storage were found to vent with flame even under 2 amp discharges at room temperature. Hence, the effects of storage give random results and no definite trends were observed. Further data are given in Table II.

The effects of the carbon cathode structure upon the safe performance of cells at 2A are shown in Figure 5. Both cells contained a stoichiometric lithium-sulfur dioxide ratio less than one. Curve 1 characterizes the cell in which the carbon capacity (9.1 Ah) was limited. The voltage curve showed a voltage polarization after 1.3 hours to -0.3 volts. At this potential the deposition of lithium at the cathode is possible for the

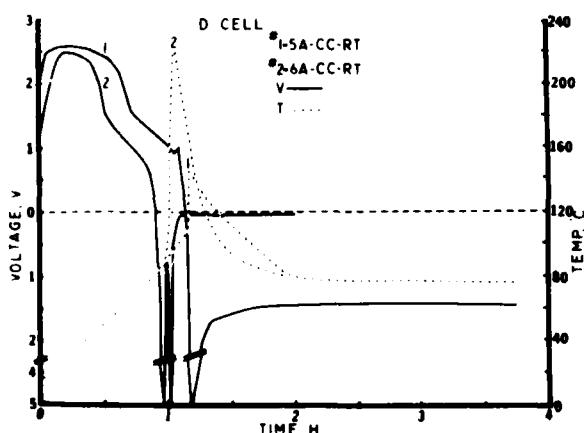


Figure 3. Voltage and Temperature for Complete 5A and 6A Discharges of "D" Cells with Li/SO₂ Ratio of One

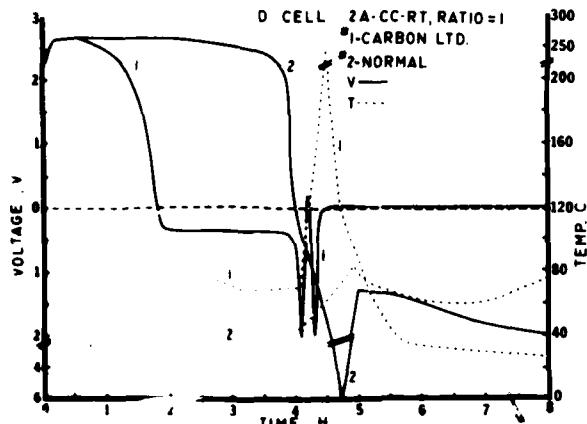


Figure 5 Voltage and Temperature for Complete 2A Discharge of "D" Cells with Different Cathodes having the same Li/SO₂ Ratio of One

same reasons presented for Figure 1. Under this condition the cell was found to increase in its lithium-sulfur dioxide ration to an unsafe region. The cell reached a temperature of 260° C and vented with flame. The cell having a carbon cathode capacity approaching that of the sulfur dioxide underwent the forced overdischarge without any abnormal incidents. Since the formulation and fabrication of the carbon cathode has not been completely defined in terms of physical parameters which include the microporosity, real surface area, and pore-size distribution, the only criteria for evaluation is its actual performance in a cell. Cells overdischarged at 1A, however, and having the same low carbon capacity did operate in a safe manner as shown in Table II.

In Figure 6, the coulombic (stoichiometric) ratio of lithium to sulfur dioxide was correlated to current for D-cells under forced overdischarge conditions. The data gathered at room temperature are representative of a number of experiments (Table II). It was shown that at currents up to 5A, the ratio should approach one. However, in Table II, it is reported that cells may be overdischarged at 6A if the carbon capacity is increased. The area designated as unstable represents mixed results in which some cells operated safely while others did not; reasons for this behavior are not immediately obvious. The unsafe region for a Li-SO₂ ratio-current relationship portrays the discharge of a poorly designed cell with regard to safety. A similar curve could be drawn for cells discharged at higher temperatures; however, at the high currents, overheating due to cell polarization and higher initial temperatures could result in cell venting. At the other extreme ambient of temperature (-40° C), the data indicates that the coulombic ratio should be less than one at higher than one amp discharge, and should

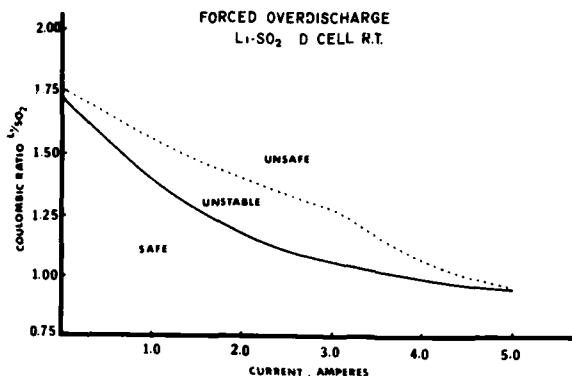


Figure 6. Correlation of Coulombic Li/SO₂ Ratios to Forced Discharge Current of "D" Cells for Predicting Safe Operation.

approach one at one amp or less. These data are summarized in Table II.

Conclusions

It has been found that to obtain a safe operating cell over a wide range of currents and at some temperatures, even under overdischarge into voltage reversal, the coulombic ratio of the lithium to the sulfur dioxide should be between 0.9 and 1.0; cells having these ratios yield less electrical capacity only when discharged at the low currents. Furthermore, the lithium anode should be the limiting component. This cell design should greatly curtail the initiation of reaction 6, which triggers cell overheating. The carbon cathode capacity also appears to influence the cell discharge safety and should be in excess of the lithium in order to prevent the apparent formation of dendritic lithium while the cell is in voltage reversal.

The free cyanide content of forced overdischarge cells (ratio, 0.92) at the 500 mA and 1A rate was found to be 0.1 mg or less after at least six hours in voltage reversal. This reduction in the amount of free cyanide from 300 mg to 0.1 mg per cell through the lower ratio cell design should alleviate the present need for special disposal methods of the lithium battery.

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